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CALCULATION OF THE DIPOLE MOMENTS OF TRI-SUBSTITUTED BENZENES

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ABSTRACT. A general method is given for the calculation of dipole moments of 1, 2, 4 tri-substituted benzenes taking into account the induced effects, similar to the treatment of Smallwood and Herzfeld for the di-substituted compounds. The calculated values are given for five compounds for which the observed values are available and a comparison is made between the calculated and observed values.

INTRODUCTION

The dipole moments of poly-substituted benzenes calculated by the simple vectorial addition of the individual group moments reveal wide divergences between the calculated and the observed values in a majority of cases. Such divergences may arise from several causes, such as, the electrostatic attractions and repulsions, the induced effects or the occurrence of mesomerism etc. In the case of the di-substituted benzenes the induced effects are computed by Smallwood and Herzfeld (1930) adopting the plane hexagonal model for the benzene ring in the substituted compounds. This has provided a valuable correction. LeFevre and LeFevre (1936, 1937) applied the method for diphenyl, coumarin, and xanthone ring systems. Each atom or group is regarded as a sphere of uniform polarisability and the induced moments are calculated by assuming that this sphere is subjected to a field which is that produced at the centre of the sphere by the primary dipole. Smyth and McAlpine (1933) calculated the induction in each bond and obtained the bond polarisabilities in terms of the bond refractions. Groves and Sugden (1937) pointed out that when the atom or group is very near the primary dipole, allowance must be made for the variation of the field over the volume of the atom and this is done by means of the method of graphical integration suggested by Frank (1935).

THEORY

In this paper the method of calculation of Smallwood and Herzfeld is extended to the case of 1,2,4 tri-substituted benzenes. The resultant moment of a tri-substituted benzene compound is regarded as comprising of (1) the vector sum of the moments of primary dipoles, (2) the mutual induction of the three primary dipoles on one another and (3) the moments induced in the $-CH$ and $-C-C$ bonds of the hydrocarbon residue by the primary dipoles.

Figure 1 represents the case of a 1, 2, 4 substituted compound. The appropriate angles and distances may be understood from figure 2. The

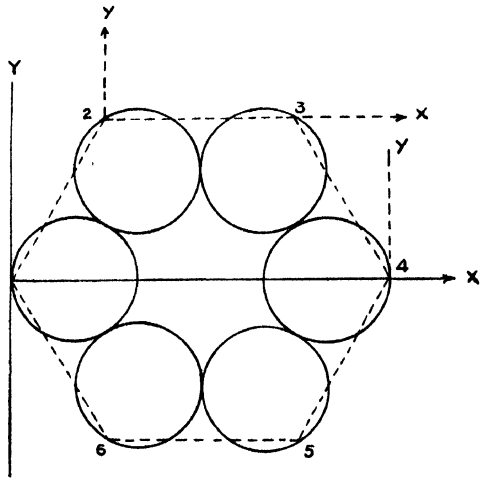

FIG. 1

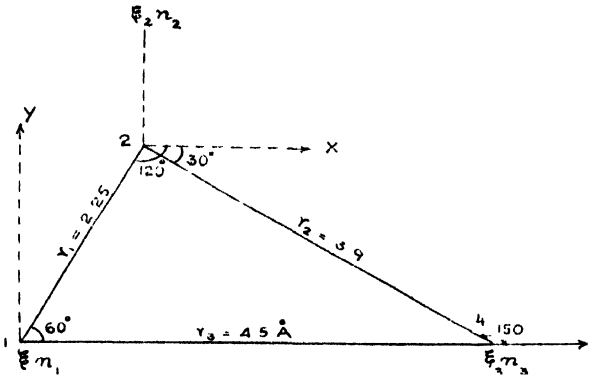

FIG. 2

notation used is the same as that of Smallwood and Herzfeld. ξ_1, ξ_2, ξ_3 represent the x-components and η_1, η_2, η_3 the y-components of m_{01}, m_{02} and m_{03} respectively. Using their equations and referring to figure 2, the interaction of the three dipoles on one another gives the following relations.

$$
\left.
\begin{aligned}
&\xi_1^1 + (a_1/4)\xi_2^1 - 2a_3\xi_3^1 - (3\sqrt{3}/4)a_1\eta_2^1 = \xi_1 \\
&(b_1/4)\xi_1^1 + \xi_2^1 - (5/4)b_2\xi_3^1 - (3\sqrt{3}/4)b_1\eta_1^1 + (3\sqrt{3}/4)b_2\eta_3^1 = \xi_2 \\
&2c_3\xi_1^1 + (5/4)c_2\xi_2^1 - \xi_3^1 - (3\sqrt{3}/4)c_2\eta_2^1 = -\xi_3 \\
&-(3\sqrt{3}/4)a_1\xi_2^1 + \eta_1^1 - (5/4)a_1\eta_2^1 + a_3\eta_2^1 = \eta_1 \\
&(3\sqrt{3}/4)b_1\xi_1^1 - (3\sqrt{3}/4)b_2\xi_3^1 + (5/4)b_1\eta_1^1 - \eta_2^1 - (b_2/4)\eta_3^1 = -\eta_2 \\
&(3\sqrt{3}/4)c_2\xi_2^1 + c_3\eta_1^1 + (c_2/4)\eta_2^1 + \eta_3^1 = \eta_3
\end{aligned}
\right\} \quad (1)
$$

where

$\alpha_1/r_1^3 = a_1$, $\alpha_1/r_2^3 = a_2$, $\alpha_1/r_3^3 = a_3$.
$\alpha_2/r_1^3 = b_1$, $\alpha_2/r_2^3 = b_2$, $\alpha_2/r_3^3 = b_3$.
$\alpha_3/r_1^3 = c_1$, $\alpha_3/r_2^3 = c_2$, $\alpha_3/r_3^3 = c_3$.

α_1, α_2 and α_3 represent the polarisabilities of the three substituent groups.

The fields of the induced moments are also considered in the above equations since we have written $\xi^1 = \xi + \xi_i$ and $\eta^1 = \eta + \eta_i$. Thus as a result of dipolar induction each ξ is modified to a certain ξ^1 and each η is modified to a certain η^1. In order to obtain the numerical values for ξ^1 and η^1 the six equations (1) are solved by the method of post-multiplication giving the values for the six variables.

The induced moments in the remaining $-CH$ groups at 3, 5 and 6 are calculated along similar lines. The values of the angles (v) and distances (r) are given in Table I. The data given in Table I are from Smallwood and Herzfeld, page 1921.

TABLE I.

Group		(3)	(5)	(6)
I	r	3.0	3.0	2.25 Å
	v	30°	−30°	−60°
II	r	2.25	1.5	3.0
	v	0°	−60°	−90°
III	r	2.25	2.25	3.0
	v	120°	−120°	−150°

The total induced effect in the $-CH$ groups at 3,5 and 6 is given as

$$\left.\begin{aligned}\Sigma\,\xi_i = 0.01320\xi_1^1 + 0.07456\eta_1^1 + 0.1021\xi^1{}_2 - 0.009324\eta^1{}_2 \\ - 0.01939\xi^1{}_3 + 0.01432\eta^1{}_3 \\ \Sigma\,\eta_i = -0.07456\xi_1^1 + 0.06624\eta_1^1 - 0.009324\xi^1{}_2 - 0.02641\eta^1{}_2 \\ + 0.01432\xi^1{}_3 + 0.1406\eta^1{}_3\end{aligned}\right\} \quad \ldots \quad (2)$$

In evaluating the induced moments in the C−C bonds, the various angles and distances used are given in Table II. These values are derived using simple trigonometrical relations from the data in Table I, assuming plane hexagonal model for the benzene ring.

TABLE II.

Group		(1)	(2)	(3)	(4)	(5)	(6)
I	r	1.3	2.6	3.438	3.138	2.6	1.3 Å
	v	30°	30°	11°	−11°	−30°	−30°
II	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	30°	−30°	−49°6′	−70°54′	−90°	−90°
III	r	1.3	2.6	3.438	3.438	2.6	1.3
	v	−150°	−150°	−169°	169°	150°	150°

The total induced moment in this case is obtained as

$$\left.\begin{aligned}\Sigma\,\xi_i^1 &= 1.3520\,\xi_1^1 + 0.2150\,\xi_2^1 - 0.7098\,\eta_2^1 + 1.3520\xi_3^1\\ \Sigma\eta_i &= -\,0.2952\eta_1^1 - 0.7098\xi_2^1 + 0.9399\eta_2^1 - 0.2952\eta_3^1\end{aligned}\right\} \quad \ldots\ (3)$$

Combining eqns. (2) and (3) the result is

$$\left.\begin{aligned}\Sigma(\xi_i^1 + \zeta_i) &= 1.3652\xi_1^1 + 0.07456\eta_1^1 + 0.3171\xi_2^1 - 0.7191\eta_2^1\\ &\quad + 1.3326\xi_3^1 + 0.01432\eta_3^1\\ \Sigma(\eta_i + \eta_i^1) &= -0.07456\xi_1^1 - 0.2290\eta_1^1 - 0.7191\xi_2^1 + 0.9135\eta_2^1\\ &\quad + 0.01432\xi_3^1 - 0.1546\eta_3^1\end{aligned}\right\} \quad \ldots\ (4)$$

Finally the resultant moment M of the molecule is given as

$$M = \sqrt{M_x^2 + M_y^2} \qquad \ldots\ (5)$$

where

$$M_x = 2.3652\xi_1^1 + 1.07456\eta_1^1 + 1.3171\xi_2^1 + 0.2809\eta_2^1 + 2.3326\xi_3^1 + 1.01432\eta_3^1$$
$$M_y = 0.9254\xi_1^1 + 0.7710\eta_1^1 + 0.2809\xi_2^1 + 1.9135\eta_2^1 + 1.0143\xi_3^1 + 0.8454\eta_3^1.$$

RESULTS

The final results for the five compounds considered, together with the observed values of Hassel and Naeshagen (1931) and Lutgert (1932) are tabulated in Table III.

TABLE III

Compound	M_{vect}	M_{eq} (5)	M'	M_{obs}	m_c value assumed
1, 2, 4 trichlorobenzene	1.64	1.24	1.40	1.25	$m_c = 1.64$
2, 4 dinitrochlorobenzene	3.26	3.11	3.19	$3.0 \pm .1$ 3.29	$m_{c1} = 1.64$ $m_{c2} = 3.75$
2, 4 dinitrobromobenzene	3.26	3.72	3.51	$3.1 \pm .1$	$m_{c1} = 1.56$ $m_{c2} = 3.75$
2, 4 dinitroiodobenzene	3.31	4.92	4.29	$3.4 \pm .1$	$m_{c1} = 1.25$ $m_{c2} = 3.75$
2, 5 dichloronitrobenzene	3.75	3.31	3.48	3.15	$m_{c1} = 1.64$ $m_{c2} = 3.75$

The values under the column (M_{vect}) are obtained by the simple vectorial addition. The second column gives the values calculated using Eqn (5). It is very difficult to judge which value of m_c (the moment of the mono-substituted compound) is to be used in the calculation since, for the same mono-substituted compound various values have been reported in the literature. For uniformity the values of Hojendahl (1929) are assumed throughout. In the case of the iodo-compound, since his value is not available the value of Walden and Werner (1929) is used. It is unfortunate that there are no values available for the tri-substituted compounds by the same authors whose values are assumed for m_c. Thus, in view of the fact that the experimental values for the mono-and the tri-substituted compounds are determined by

different authors and since the values are liable to vary, the calculated and observed values may not be expected to agree closely. From Table III we note that a closer approximation to the observed values is obtained by using Eqn (5) than in the case of M_{vect} for three of the compounds studied (1, 2, 4 trichlorobenzene, 2, 4 dinitrochlorobenzene and 2, 5 dichloronitrobenzene). The polarisabilities of the groups increase as we go from chloro to bromo- to the iodo-compound and hence the induced effects also increase in the same direction. As we see from the table, the deviation between the calculated and the observed values also increases in the same direction.

In the above calculations, a correction for the dielectric constant of the internuclear space is also considered. LeFevre and LeFevre (1937) pointed out that the calculated induced moment must be reduced by the factor $(\varepsilon+2)/3\varepsilon$ (ε being the dielectric constant of the internuclear space) in order to obtain the actual induced moment. The value of ε is obtained as 2.40 from measurements of the variation of the dielectric constant of benzene with pressure. Groves and Sugden also remarked that little error will be introduced by assuming $\varepsilon=2.40$ in the case of aromatic compounds. The reduction factor turns out to be 4.4/7.2. The values obtained when this correction is applied are given under the column headed M' in Table III. The difference between M_{eq} (5) and M_{vect} gives the induced moment. This difference multiplied by the factor 4.4/7.2 gives the actual induced moment. This is added algebraically to M_{vect} to give the value under M'. By this process, the agreement with the observed value is improved for all the compounds studied except 1, 2, 4 trichlorobenzene where the induced contribution to the moment is considerably large.

The assumptions in the above method and other errors will have to be clearly stated. (1) The assumption that the dipoles are situated at the circumference of the carbon atoms to which the groups are attached, is an approximation. Smyth (1934) remarks that a consideration of the location of the centre of gravity of the charges assignable to the carbon halogen portion of the molecule in the halogenated compounds indicates the most probable location of the principal dipole to be approximately 7/8 of the distance from the carbon nucleus to the halogen nucleus. But the first assumption is adopted, as otherwise the calculations become extremely complicated. (2) The distances between the various groups enter in the third power in the equations used for computing the induced moment, Hence a small error in the distance may cause a relatively large error in the final value of the moment. (3) The method has not taken into account the variation of the field of the dipole over the volume of the atom or group in which the moment is induced, since the distances under consideration are all greater than 1 A.U. The equation, assuming proportionality between the induced moment and the field of the primary dipole ($m_i=\alpha E$), breaks down at close distances. (4) Rotation round the bonds may also affect the